電気材料技術雑誌 第10巻第2号
J. Soc. Elect. Mat. Eng. Vol. 10, No. 2, 2001

Time-Resolved Characteristics of Second-Order Processes for Formation of Free Polarons in Conjugated Polymers

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Photoconductivity of conjugated polymers is an important property that works in many applications of the materials. It is a complex physical phenomenon, depending on many fundamental things, and it is worth to be studied by using different techniques. Up to now there exist two main approaches for description of the photoconductivity, one of them considering absorbed light induced inter-band transitions, like in inorganic semiconductors, and the other treating the photoconductivity as a result of reactions with participation of excited species formed under the light absorption [1]. In this respect, the last approach is similar to that in molecular crystals where excitons are formed primarily, and then their autoionization and electron-transfer reactions occur. However, recent studies carried out by pump-and-probe technique have shown that in contrast to molecular crystals charge carriers appear within a part of ps after the light absorption [2-5]. In the work such a conclusion was arrived at by measurement of the time-resolved formation of polaron pairs within the picosecond time domain by probing changes of the cw-photocurrent instead of the light absorption [3]. In connection with this fact, one has to note that the appearance of charged species in the material is necessary but not sufficient condition for the cw-photocurrent.They must be free to drift under the action of an external electric field, and show a certain shift by the field during their lifetime. However, positive and negative charge carriers in molecular solids being formed in pairs remain in the mutual Coulomb field, and recombine geminately [6-9]. That is a consequence of a low mobility of charge carriers or polarons. For geminately recombining polaron pairs the net shift of charges is zero. Only a part of the pairs manages to dissociate and contribute to the cw-photocurrent.

Activated dissociation of polaron pairs does not appear to be the only way of free carrier formation. Our recent results [3] obtained on substituted polythiophene and poly(*p*-phenylenevinylene) have shown that at the laser pulse excitation the photoconductivity appears, which does not depend on the temperature. According to the model primarily formed charge carriers belong to polaron pairs, and they can take part in the photoconductivity only if

geminate recombination is prevented. These primarily formed polaron pairs contain polarons with higher (about 0.2 cm^2/Vs) and temperature independent mobility [3]. At low temperature the pairs cannot dissociate, and it was conjectured that free polarons appear as a result of inter-pair recombination: Two charges from neighbor pairs recombine leaving two remaining charges at higher inter-charge distance and thus increasing their chance to be outside the Onsager radius and get free.

In the present work we studied processes responsible for the formation of free polarons (free charge carriers) in samples of a typical conjugated polymer, poly(2,5-dioctyloxy-*p*-phenylenevinylene) (OO-PPV), under laser light (wavelength 400 nm) excitation by a new technique based on the correlated action of two 150 fs laser pulses with controlled delay time between them. The technique is selectively sensitive to the second order processes with participation of intermediate active species having the lifetime within the range of delay times used. A scenario of the processes is suggested, which involves primary formation of pretrapped polaron pairs, termalization of the pairs, and inter-pair recombination.

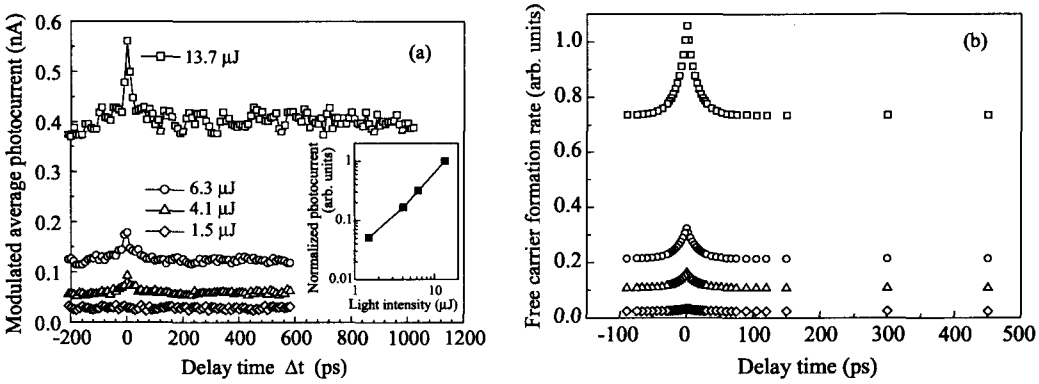

Fig. 1: (a) Experimental dependencies of the modulated average photocurrent, measured by a lock-in amplifier at the modulation frequency equal to 20 Hz, on the delay time at different light pulse intensities. The gap between electrodes=10μm, and V=18V (E=18kV/cm). *Inset*: The peak of the modulated average photocurrent at Δt=0 plotted as a function of the light intensity. (b) The same as (a) but computer calculated by Eqs. (1) and (2).

Figure 1(a) presents similar results obtained on an OO-PPV sample measured by the lock-in amplifier (Stanford Research System SR830) with the first pulse modulation. The results were obtained on the sample prepared by casting from toluene solution and have permitted to get more information. The modulated average photocurrent was measured from zero delay time up to delay time Δt=1 ns at different intensity of the light pulses as indicated in the figure. The inset of Fig.1 shows the dependence of the maximum average photocurrent (at zero delay time) on the intensity of the light pulses that becomes superlinear at higher than 4 μJ/pulse.It is evident that the width of the peaks does not depend on the intensity of the

light, and the half-width at $1/e$ of the maximum intensity is about 14 ps.

Kinetic equation that would be able to describe formation and recombination of polaron pairs P_2 can be written as follows:

$$\frac{dP_2}{dt} = g(t) - (k_{g2} + k_{th})P_2 - k_{22}P_2^2 \tag{1}$$

where at t=0 P_2=0. Here $g(t)$ is the rate of formation of polaron pairs. In the two-correlated-pulse regime $g(t) = g_1 e^{-\left(\frac{t-\Delta t}{t_0}\right)^2} + g_2 e^{-\left(\frac{t}{t_0}\right)^2}$, where t_0 is the width of the pulse, Δt is the delay time; P_2 is a density of thermalized polaron pairs. The constant k_{g2} is the rate constant for geminate recombination, k_{22} is the rate constant for random recombination (inter-pair recombination), and k_{th} is the rate constant for the dissociation of polaron pairs and the formation of free polarons.

Two terms in Eq. (1) may be considered as those responsible for the appearance of free charge carriers. They are (i) the term $k_{22}P_2^2$ (inter-pair random recombination of two charges from different pairs leaves two other charges at higher inter-charge distance and gives them a chance to get free), and (ii) the term $k_{th}P_2$ describing thermal and electrical field assisted dissociation of polaron pairs.

The next kinetic equation, which works for accumulation of free polarons p after the action of two correlated pulses, can be written as follows:

$$\frac{dp}{dt} = \beta_1 k_{22}P_2^2 + k_{th}P_2 \tag{2}$$

where at t=0, p=0; $\beta_1 < 1$ is the yield of free charge carriers formed per one inter-pair recombination event. Solution of the system of Eqs. (1) and (2) permits to get the yield of free charge carriers formed under photo excitation that is directly proportional to the value of p obtained by that way. We assume that the photocurrent measured experimentally is directly proportional to p.

We solved the system of Eqs. (1) and (2) by computer simulation and arrived at the dependencies shown in Fig.1 (b). The values of the rate constants were regulated in order to fit in general features of experimental curves. The most important parameters in the experimental curves, which appeared to be important for choosing the rate constants, were (I) the half-width of the peak connected with the lifetime of the species taking part in a second order process, (II) the maximum relative change of the photocurrent that corresponds to an increase of the delay time from zero to a much longer value. The values of the rate constants were calculated on the basis of these parameters:$k_{1g}+k_{th}=1/\tau_p=6.7\times10^{10}\mathrm{s}^{-1}$ (it is the experimental value obtained from the half-width of the peak in the Fig.1(a)), $k_{22}=4\times10^{-9}\mathrm{cm}^3/\mathrm{s}$ (but it was revealed that the results were not sensitive to values of k_{22} if the latter are smaller than indicated one). The maximum relative change of the photocurrent with the delay time was revealed to be very critical for choosing the ratio S of probabilities of formation of free carriers from a recombination

event and from dissociation of polaron pairs $S = \frac{\beta_1}{k_{th}\tau_p}$. The ratio was calculated as S=20, and on basis of it we have taken arbitrarily β_1=0.1 and k_{th}=3.3×10^{8}s^{-1}. Calculations were done for polaron pair generation rates g_1=g_2 from 4.8×10^{30} to 4.4×10^{31}cm^{-3}s^{-1} corresponding to light pulse power from 1.5 to 13.7 μJ/pulse at the assumption of the quantum yield of polaron pair formation to be 0.2 and extinction coefficient to be 5×10^{4}cm^{-1}. Figure 1(b) shows the dependencies of the free carriers formation rate on delay time calculated for the same light intensity as measured in experimental work. The calculated changes of photocurrent as a function of light intensity fit satisfactorily to the experimental result as shown in Fig. 1(a). The peak having the half-width of about 14 ps corresponds to that observed in experimental work as well.

In conclusion, the technique based on the action of pairs of correlated light pulses with a controlled delay time between them was applied successfully for studying second order processes responsible for formation of free charge carriers in conjugated polymers. We worked with poly(2,5-dioctyloxy-*p*-phenylenevinylene) (OO-PPV), have performed time-resolved experiments within the picosecond time domain, and have got direct evidence on existence of intermediate states preceding free charge carriers at the photo excitation of conjugated polymers. They are shown to take part in second order processes responsible for the generation of free charge carriers in conjugated polymers at high excitation density.

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